Hidden Boron Catalysis: Nucleophile-Promoted Decomposition of HBpin

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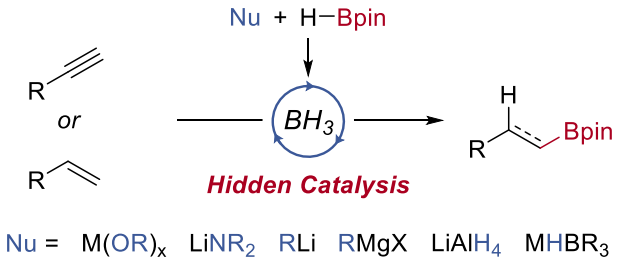
Supporting Information

ABSTRACT: Simple nucleophiles, with structural similarities to known hydroboration catalysts, can readily mediate the formation of BH_3 and borohydride species from pinacolborane (HBpin). Alkyne and alkene hydroboration reactions were successfully mediated by nucleophiles through BH_3 generation, with BH_3-catalyzed hydroboration found to dominate catalysis. NMR spectroscopy and kinetic analyses showed that the nucleophiles NaO^{t}Bu, Na[N(SiMe$_3$)$_2$], ^{n}Bu$_2$Mg and ^{n}BuLi only promoted the formation of BH_3 and were not 'true' hydroboration catalysts.

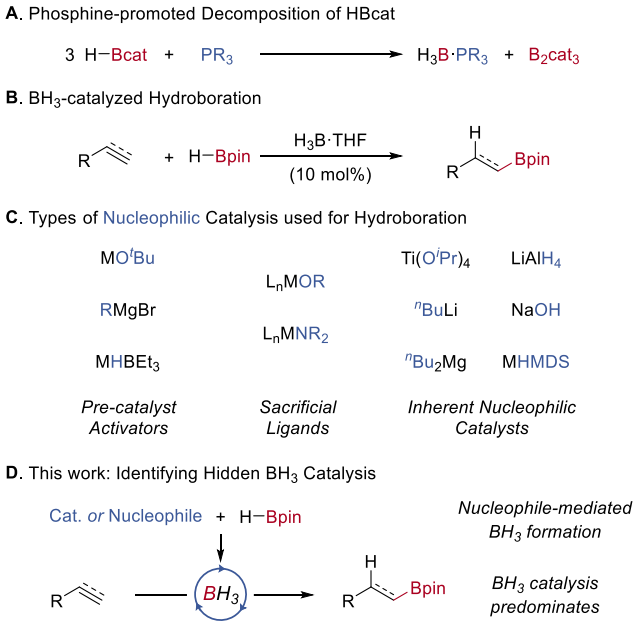


The need for sustainable catalysis has necessitated the development of a wide range of first-row transition metal and main-group complexes for catalysis with the hydroboration of carbonyls, imines, alkynes and alkenes with pinacolborane (HBpin) or catecholborane (HBcat) acting as an exemplar reaction.[1-4] However, the formation of BH_3 has been observed in metal-catalyzed hydroborations with HBcat, where hydroboration by BH_3 competed with the metal-catalyzed reaction.

In rhodium-catalyzed alkene hydroboration reactions with HBcat, the phosphine ligand of the catalyst was found to initiate the decomposition of HBcat to BH_3 (Scheme 1A).[5-8] In other cases, the 'catalysts' were proposed to only mediate the decomposition of HBcat to BH_3.[9-12] BH_3 has been used to catalyze the hydroboration of alkynes with HBcat,[13] and alkynes and alkenes with HBpin (Scheme 1B).[14] Whilst the nucleophile-promoted formation of BH_3 from HBcat has received significant attention and is routinely controlled for,[6-12] the formation of BH_3 from HBpin is not. The inherent differences in stability of HBcat and HBpin prevents the extrapolation of HBcat decomposition to HBpin and very rarely have control reactions been performed for BH_3 when using HBpin.[15] As the majority of new catalytic hydroboration systems contain nucleophilic motifs, it is necessary to exclude nucleophile-promoted BH_3 formation from 'true' catalysis by the metal/metalloid species. The nucleophilic motifs can be separated into three classes: pre-catalyst activators,[15-22] sacrificial ligands[23-25] and inherent nucleophilic catalysts (Scheme 1C).[26-31] To distinguish between 'true' catalysis and BH_3 catalysis for reactions using HBpin it was necessary to:

1. Identify nucleophile-promoted BH_3 formation.
2. Determine if BH_3 forms under catalysis conditions.
3. Compare the rate of reaction to that of BH_3 catalysis.

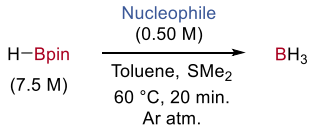
Scheme 1. The Roles of Nucleophiles and BH_3 in Hydroboration Catalysis



We began by screening nucleophiles with similar motifs to known hydroboration systems to determine their ability to mediate the decomposition of HBpin to BH_3 (Table 1). Ti(O^{i}Pr)$_4$ was used by Burgess to question the veracity of the Ti-catalyzed hydroboration of alkenes with HBcat.[11] Reaction of Ti(O^{i}Pr)$_4$ with HBpin gave 0.30 M BH_3 as observed by ^{11}B NMR spectroscopy (Entry 1). Sodium and potassium *tert*-butoxide have been shown to form BH_3 when mixed with HBpin and have been used as activators in hydroboration catalysis.[15-18] All metal alkoxides gave similar amounts of BH_3 formation (Entries 2-4).

Organolithium and Grignard reagents have been used as pre-catalyst activators.[19-20] Reaction of MeLi and MeMgBr with HBpin both showed formation of BH_3 (Entries 5 and 6). Likewise, $NaHBEt_3$ has been used as an activator and was observed to promote BH_3 formation (Entry 7).[21-22] Alkoxides, amides, NaOH, ^{n}Bu$_2$Mg, ^{n}BuLi and $LiAlH_4$ have all been proposed to be active hydroboration catalysts[26-31] or used as sacrificial ligands.[23-25] All promoted BH_3 formation (Entries 8-13). [BH_3] was shown to remain constant after 2 hours by using ^{n}BuLi as an exemplar (SI, Table S1). Only NaOTf did not form BH_3 (Entry 15).

Table 1. Quantifying BH_3 Formation from the Reaction of Nucleophiles with HBpin

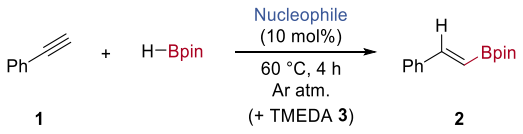


Entry	Nucleophile / Catalyst	[BH_3] (M)
1	$Ti(O^iPr)_4$	0.30
2	KO^tBu	0.02
3	NaO^tBu	0.02
4	LiO^tBu	0.03
5	MeLi	0.02
6	MeMgBr	0.01
7	$NaHBEt_3$	0.03
8	$Na[N(SiMe_3)_2]$	0.02
9	LDA	0.06
10	NaOH	0.01
11	^{n}Bu$_2$Mg	0.07
12	^{n}BuLi	0.04
13	$LiAlH_4$	0.18
14	$LiBH_4$	0.01
15	NaOTf	0.00

Conditions: Nucleophile (0.12 mmol, 0.50 M), HBpin (1.8 mmol, 7.5 M), SMe_2 (0.12 mmol), toluene (0.24 mL), 60 °C, 20 min. Conversion determined by ^{11}B NMR spectroscopy.

Whilst an extensive range of nucleophiles reacted with HBpin to give BH_3, their ability to form sufficient amounts to catalyze a hydroboration reaction required confirmation. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) **3** forms air- and moisture stable mono- and bis-adducts with BH_3,[32] so would serve as a BH_3 indicator; the adducts were observable by ^{11}B NMR spectroscopy even after work-up. The $H_3B{\cdot}SMe_2$-catalyzed (10 mol%) hydroboration of phenylacetylene **1** gave the alkenylboronic ester **2** in 94% yield (Table 2, Entry 1, left). The addition of TMEDA **3** (10 mol%) significantly inhibited hydroboration (Entry 1, right). The $H_3B{\cdot}$TMEDA adducts were poor catalysts for the hydroboration at 60 °C, compared to $H_3B{\cdot}SMe_2$ (SI, Table S2). Control experiments showed no interaction between TMEDA **3** and HBpin at 60 °C (see SI). Nine nucleophiles were found to mediate the hydroboration of phenylacetylene **1** with HBpin (Entries 2-10). In all cases TMEDA **3** was found to effectively inhibit alkyne hydroboration and $H_3B{\cdot}$TMEDA was observed by ^{11}B NMR spectroscopy in all cases.

Table 2. Inhibition of Alkyne Hydroboration by TMEDA



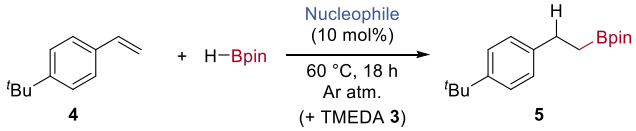
1 **2**

Entry	Nucleophile / Catalyst	**2** (%) No TMEDA **3** (0 mol%)	**2** (%) + TMEDA **3** (10 mol%)[a]
1	$H_3B{\cdot}SMe_2$	94	10
2	$NaHBEt_3$	61	3[b]
3	$LiAlH_4$	51	3
4	NaOH	41	1
5	NaO^tBu	59[c]	1[c]
6	$Na[N(SiMe_3)_2]$	29	0
7	MeMgBr	60	1
8	^{n}BuLi	53	1[d]
9	$Ti(O^iPr)_4$	51	5[d]
10	^{n}Bu$_2$Mg	81	11[d]

Conditions: **1** (1.0 mmol), nucleophile (0.10 mmol), HBpin (1.5 mmol). Yields determined by ^{1}H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene). [a]TMEDA **3** (0.10 mmol). [b]TMEDA (0.60 mmol). [c]18 hours. [d]TMEDA (0.30 mmol).

As the hydroboration of alkenes is also catalyzed by BH_3 (Table 3, Entry 1),[14] the selected nucleophiles were tested in the hydroboration of *tert*-butylstyrene **4** with HBpin. Similar results were observed to those using phenylacetylene **1**. All nucleophiles efficiently promoted the hydroboration of *tert*-butylstyrene **4**, and hydroboration was inhibited by TMEDA **3** (Entries 2-10). $H_3B{\cdot}$TMEDA was observed in all cases and, once again, the role of the nucleophile was to promote BH_3 formation.

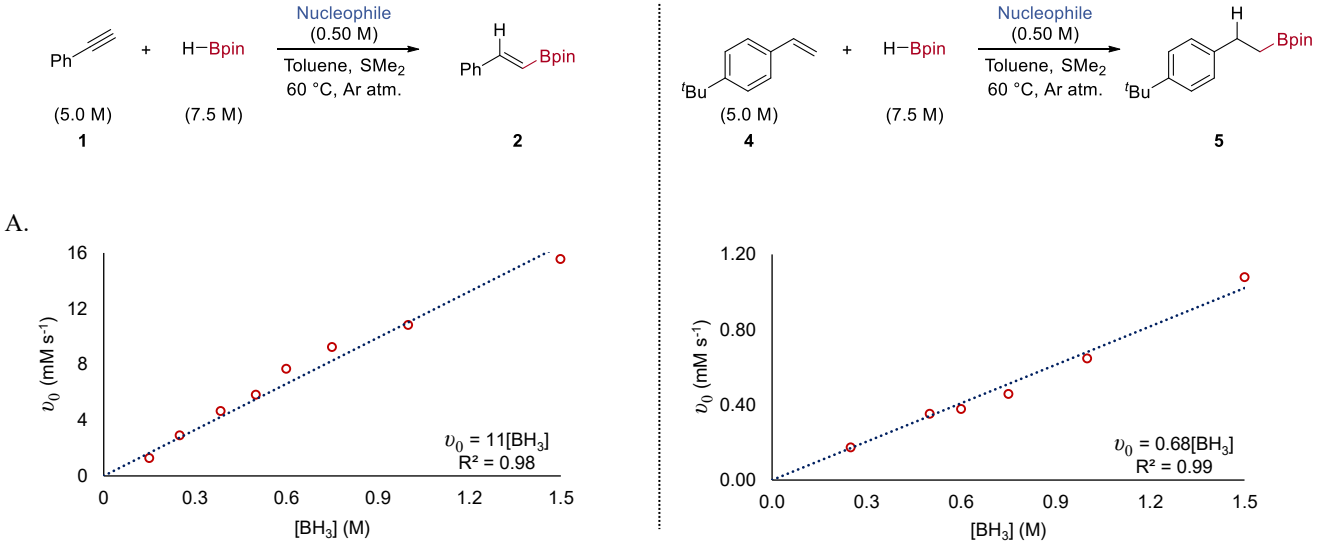
Table 3. Inhibition of Alkene Hydroboration by TMEDA



4 **5**

Entry	Nucleophile / Catalyst	**5** (%) No TMEDA **3** (0 mol%)	**5** (%) + TMEDA **3** (20 mol%)[a]
1	$H_3B{\cdot}SMe_2$	67	5
2	$NaHBEt_3$	81	43
3	$LiAlH_4$	81	5
4	NaOH	28	7
5	NaO^tBu	71	10
6	$Na[N(SiMe_3)_2]$	72	12
7	MeMgBr	55	21
8	^{n}BuLi	30	26
9	$Ti(O^iPr)_4$	73	10
10	^{n}Bu$_2$Mg	85	22

Conditions: **4** (1.0 mmol), nucleophile (0.10 mmol), HBpin (1.5 mmol). Yields determined by ^{1}H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene). [a]TMEDA **3** (0.20 mmol).



B.

Entry	Nucleophile / Catalyst	v_0, Hydroboration of **1** (mM s^{-1})	v_0, Hydroboration of **4** (mM s^{-1})	$[BH_3]_{calc}$ using **1** (M)	$[BH_3]_{calc}$ using **4** (M)	$[BH_3]_{obs}$ (M)[a]
1	$H_3B{\cdot}SMe_2$	5.8	0.35	N/A (0.50 M $H_3B{\cdot}SMe_2$)		
2	NaO^{t}Bu	0.15	0.013	0.01	0.02	0.02
3	Na[N(SiMe$_3$)$_2$]	0.15	0.022	0.01	0.03	0.02
4	$LiAlH_4$	2.1	0.22	0.19	0.32	0.18
5	^{n}Bu$_2$Mg	2.0	0.11	0.18	0.16	0.07
6	^{n}BuLi	3.6	0.13	0.33	0.19	0.04
7	Et_3B	1.7	-	0.15	-	-
8	Et_3B and $H_3B{\cdot}SMe_2$[b]	2.0	-	0.18	-	-
9	H-*B*-9-BBN	>32	0.18	N/A (0.50 M H-*B*-9-BBN)		

Figure 1. A. Calibration gradients of initial rates of reaction (v_0) plotted against [BH_3] (M) for the hydroboration of 1 (left) and 4 (right). B. Comparison of the calculated and observed BH_3 concentrations. Conditions: 1 or 4 (2.0 mmol, 5.0 M), nucleophile (0.20 mmol, 0.50 M, 10 mol%), HBpin (3.0 mmol, 7.5 M), SMe_2 (0.20 mmol, 0.50 M), toluene (0.40 mL), 60 °C, 20 min. prior to the addition of substrate 1 or 4 (then alkyne 1.5 h; alkene 22 h). Yields determined by ^{1}H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene, 0.10 mmol).[a] From Table 1. [b]Et_3B (0.09 M) and $H_3B{\cdot}SMe_2$ (0.07 M).

The addition of TMEDA **3** to the hydroboration reactions clearly indicated that BH_3 was formed under reaction conditions. However, TMEDA **3** could also inhibit 'true' catalysis by coordination to the metal or by altering aggregation states.[33-35] To distinguish 'true' catalysts from those which only decompose HBpin to BH_3, the rates of the BH_3-catalyzed hydroborations of alkynes and alkenes (v_0) were plotted against [BH_3] loading to generate a calibration gradient (Figure 1A). The rates of the nucleophile-promoted hydroboration reactions were then measured and compared to this (Figure 1B). If the calculated BH_3 concentration ($[BH_3]_{calc}$) matched the observed BH_3 concentration ($[BH_3]_{obs}$, from Table 1), it would suggest that the nucleophiles were not active catalysts but simply promoting the decomposition of HBpin to BH_3. Direct comparison between Table 1 and Figure 1B was enabled by matching the reaction conditions and adding the substrate after 20 minutes; the same point at which $[BH_3]_{obs}$ was measured in Table 1.

NaO^{t}Bu and Na[N(SiMe$_3$)$_2$] exhibited comparable $[BH_3]_{obs}$ and $[BH_3]_{calc}$ for both the alkyne and alkene hydroboration reactions (Figure 1B, Entries 2 and 3), suggesting these are not 'true' catalysts but promoters of HBpin decomposition to BH_3. For $LiAlH_4$, $[BH_3]_{calc}$ of alkyne hydroboration matched $[BH_3]_{obs}$, but $[BH_3]_{calc}$ was higher than expected for alkenes (Entry 4). Presumably, AlH_3 is formed in this case,[36] introducing a complementary, additional, aluminum-catalyzed hydroboration.[26]

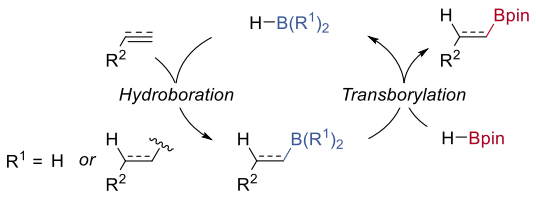
When ^{n}Bu$_2$Mg was tested, $[BH_3]_{obs}$ was lower than $[BH_3]_{calc}$ (Entry 5) suggesting that ^{n}Bu$_2$Mg may be an active catalyst. However, ^{n}Bu$_3$B (0.09 M) was also observed by ^{11}B NMR spectroscopy. The sum of $[^nBu_3B]_{obs}$ and $[BH_3]_{obs}$ equaled $[BH_3]_{calc}$. Although trialkylboranes have not been reported to catalyze hydroboration reactions, they are known to redistribute to catalytically active dialkyl- and monoalkylboranes,[37-38] e.g. ^{n}Bu$_2$BH and ^{n}BuBH$_2$, in the presence of BH_3.[39] Hydroboration using Et_3B (10 mol%) was successful (Entry 7), presumably through redistribution with HBpin to form $R_{3-n}BH_n$ species, albeit at a much lower rate than that using BH_3. Using a solution of BH_3 and Et_3B that mimicked the concentrations of BH_3 and ^{n}Bu$_3$B formed under catalysis conditions gave an equal rate of reaction to the ^{n}Bu$_2$Mg-mediated hydroboration of alkynes (Entry 8). Therefore, ^{n}Bu$_2$Mg is not a 'true' catalyst for the hydroboration of alkynes and alkenes but merely a nucleophile.

$[BH_3]_{obs}$ for ^{n}BuLi was lower than $[BH_3]_{calc}$ and the hydroboration of alkynes had a higher $[BH_3]_{calc}$ compared to alkenes (Entry 6). Again, this suggested that ^{n}BuLi was an active catalyst.

^{13}C NMR spectroscopy showed that ^{n}BuLi was fully consumed in the reaction of ^{n}BuLi with HBpin. Furthermore, $LiBH_4$ was observed by ^{11}B and ^{7}Li NMR spectroscopy and was the only lithium species present, inferring that the hydroboration reactions were not catalyzed by ^{n}BuLi. $^{n}BuH_2B{\cdot}SMe_2$ was also observed by ^{11}B NMR spectroscopy, suggesting that $^{n}Bu_2BH$ and $^{n}BuBH_2$ were formed, along with $^{n}Bu_3B$. The difference between $[BH_3]_{calc}$ for alkynes and alkenes is presumably due to the different rates of hydroboration using mono- and dialkylboranes, and BH_3 (Entries 1 and 9).[40]

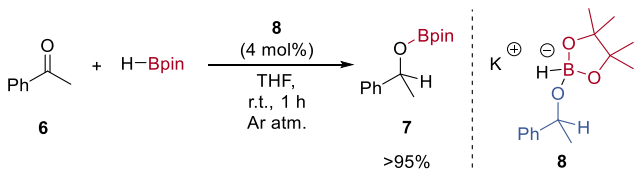
Borane-catalyzed hydroboration is proposed to proceed by an initial hydroboration to give an alkenyl- or alkylborane intermediate which undergoes transborylation[38,41] with HBpin to give the boronic ester product and regenerate the borane catalyst (Scheme 2).

Scheme 2. Proposed Borane-catalyzed Hydroboration Mechanism



Ketone hydroboration is often used as a basis to test new catalyst structures.[2-4] However, Clark showed that ketone hydroboration with HBpin was mediated by NaO^{t}Bu.[17] Nucleophilic addition of NaO^{t}Bu to HBpin gave a trialkoxyborohydride, which is known to reduce ketones.[42] Borohydride addition to a ketone formally gives an alkoxide, which reacts with HBpin to form another trialkoxyborohydride, propagating the reaction. To confirm Clark's mechanism, and show its applicability to other nucleophiles, the hydroboration of acetophenone **6** was investigated. Whilst BH_3 would successfully mediate the hydroboration of acetophenone **6**, the yield was much lower than any of the nucleophile-mediated reactions (SI, Table S4). Therefore, nucleophile-mediated ketone hydroboration does not proceed by BH_3 catalysis. In the nucleophile-promoted decomposition reactions, borohydride species were observed in addition to BH_3. Nucleophile-promoted decomposition of HBpin must proceed by the initial formation of a hydridic boron 'ate' species, from nucleophilic addition to HBpin (e.g. $[NuHBpin]^-$). Trialkoxyborohydride **8** (the product of hydride transfer to acetophenone) was prepared and shown to be an active catalyst for the hydroboration of acetophenone **6** (Scheme 3). This supports Clark's mechanism and demonstrates this mechanism is applicable to the other nucleophiles studied. It is possible that this mechanism is operative in the hydroboration of other carbonyl derivatives.

Scheme 3. Trialkoxyborohydride-Mediated Acetophenone Hydroboration



Conditions: **6** (1.0 mmol), **8** (0.20 M in THF, 0.040 mmol), HBpin (1.5 mmol). Yield determined by ^{1}H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene, 0.10 mmol).

The hydroboration of alkynes, alkenes and ketones with HBpin can be effectively mediated by simple nucleophiles. The results suggest that the reactions proceed through nucleophile-promoted decomposition of HBpin. BH_3 and borohydride species are formed by decomposition and these are active catalysts for the hydroboration of alkynes and alkenes, and ketones, respectively. For carbanion-containing systems, the decomposition is more complex, forming multiple borane species, all of which are potentially active hydroboration catalysts. Any future hydroboration catalysts should be rigorously tested to confirm that the decomposition of HBpin does not occur, particularly non-enantioselective catalysts and those that exhibit the same regioselectivity as BH_3-catalyzed hydroboration or borohydride reduction. The addition of TMEDA and ^{11}B NMR spectroscopy both offer means of observing R_3B (R = H, alkyl or alkenyl) in catalyzed hydroboration reactions. However, it should be noted that, even in BH_3-catalyzed reactions, observation of these intermediates may be challenging as transborylation from R_3B to RBpin is fast and results in very low R_3B concentrations.

ASSOCIATED CONTENT

Supporting Information. General experimental information, experimental setup and procedures, reaction monitoring, NMR spectra and associated references. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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